FINAL REPORT
on an investigation of
THE THREE BODY PROBLEM IN ATOMIC PHYSICS

by

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covering the period of 21 February 1961 to 20 February 1963.

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ABSTRACT:

The report gives a summary of several investigations in two-electron spectroscopy carried out under Contract AF 61(052)-510 during the two-year period of 21 February 1961 to 20 February 1963.

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A. Introduction

1. Our research on the three-body problem in atomic physics started in 1958 with the publication of the paper

1. C.L. Pekeris, Ground State of Two-Electron Atoms, Phys. Rev. 112, 1649 (1958).

In this paper a new method was developed for the solution of the Schrödinger wave equation for two-electron atoms. Instead of using the sides of the triangle of the three particles as independent coordinates, a new set of perimetric coordinates was introduced. These are linear combinations of the former coordinates, so chosen as to allow fixed limits for each.

The second deviation from the classical Hylleraas variational method was to substitute directly into the differential Schrödinger wave equation the development of the wave function into a triple Laguerre series. The condition imposed on the solution was thus the vanishing of the Schrödinger operator rather than the vanishing of the variation of the Lagrangian.

This led to a recursion relation between the coefficients in the expansion, which contained 33 terms. The capabilities of electronic computers to handle such complex relationships was demonstrated for the first time in the case of this recursion relation. The energy eigenvalue was obtained as a root of the determinant resulting from the recursion relation.

In this first publication we showed that it is feasible to solve determinants of orders n up to 214.

The principal numerical result of this investigation was a term-value for the ground state of Helium accurate to within 0.01 cm^{-1}. The experimental accuracy of this state was 0.15 cm^{-1}, as measured by Herzberg.

2. In the second paper of this series,

2. C.L. Pekeris, 1^1S and 2^3S States of Helium, Phys. Rev. 115, 1216 (1959),

an accuracy 0.001 cm^{-1} in the term-values was aimed at. For the first time we showed that it is possible to solve determinants of an order n as high as 1078. In the case of the 2^3S state of Helium, an order $n = 715$ was sufficient to render an accuracy in the nonrelativistic term-value of 0.001 cm^{-1}. Such

an accuracy is, of course, way beyond the experimental uncertainty in the term-value, which is around 0.05 cm^{-1}. However, our aim in these refined calculations was to obtain high accuracy in the wave functions also.

One of the points of interest in this context was the value of the electron density at the nucleus for the 2^3S state. Vernon Hughes and his collaborators were then making very accurate measurements of the hyperfine splitting of the 2^3S level of He^3, which promised to throw light on the structure of the nucleus of He^3. For this purpose it was necessary to have a value for the electron density of the origin accurate to one part in 10^8. This was actually achieved in publication number 5 discussed below.

B. Research Done under this Contract.

3. The first paper published under this contract AF 61(052)-510 was

3. C.L. Pekeris, 1^1S, 2^1S and 2^3S States of Li^+, Phys. Rev. 126, 143 (1962).

It originated in an attempt to provide a theoretical basis for the extremely accurate measurements made by Herzberg and Moore of the levels of the 2^1S and 2^3S states of Li^+. Their experimental accuracy was ± 0.10 cm^{-1}, even better than the value ± 0.15 cm^{-1} achieved by Herzberg for the 2^1S state of Helium. We were able to obtain a perfect check with their experimental term-value of the 2^3S state. However, for the 2^1S level we obtained a value which disagreed with their experimental value by the enormous gap of 1300 cm^{-1}. We arrived at the conclusion that the 8517.4 Å line which they measured with extreme accuracy was not the 2^1S - 2^1P transition. According to our calculations, that line should be found at 9584 Å. Unfortunately, neither Herzberg and Moore at Ottawa, nor Series and Willis at Oxford, felt that they could overcome the low plate sensitivity at 9584 Å and detect our predicted line.

Our prediction was verified experimentally in the summer of 1962 by

Y. G. Toresson and B. Edlén, the 1s2s ^1S Level of Li^+, Arkiv för Fysik, Band 23 No. 11, 117 (1962).

They obtained a term value for the 2^1S level of Li^+ which was "in perfect agreement" with our calculated value.

4. Our next investigation,

4. C.L. Pekeris, B. Schiff, and H. Lifson, Fine Structure of the 2^3P and 3^3P States of Helium, Phys. Rev. 126, 1057 (1962),

was aimed at furnishing a theoretical interpretation for the very accurate fine-structure measurements made by Lamb in 1957. These measurements have since been refined by members of Lamb's school. The calculations of the P-states are much more difficult than the S-states, the first realistic attempt having been made only as late as 1959 by Traub and Foley. In this investigation we achieved an accuracy considerably beyond that of Traub and Foley, but still not comparable to the experimental accuracy. However, if our calculated values are extrapolated to determinants of order ∞, then the indications are that the experimental values will be substantiated. Further work on this problem is now going on, and the pace of progress in this topic will be accellerated by April 1963 when our 1604-A - 160-A computer system will get into full swing.

5. The investigation

5. C.L. Pekeris, 1^1S, 2^1S and 2^3S States of H^- and of He, Phys. Rev. 126, 1470 (1962),

gives a vast amount of new results which have accumulated in the course of our studies of two-electron spectroscopy. It starts with furnishing evidence to the effect that the negative hydrogen ion has only one bound state. This question has been in the air for more than a decade and we are convinced that there is no more than one bound state.

A second topic treated was the electron density at the nucleus of the 2^3S state of Helium. V. Hughes and his school made more accurate measurements of the hyperfine structure of the 2^3S state of Helium. They achieved an accuracy of 2 parts in 10^7. With our value of the electron density at the nucleus published in reference 2, they concluded that their measurements indicate a disagreement of one part in 10^5 with the hyperfine structure theory of Sessler and Foley.

We have therefore extended our calculations to an order 1078. The results completely substantiated our previously published value, and with it Hughes' experimental evidence of a discrepancy with the current theory of the hyperfine structure of He^3.

A third topic discussed in this paper was the question of getting lower bounds for the energy levels of the 1^1S and 2^3S states of Helium. Ever since the appearance of our paper in 1958, Professor Salpeter of Cornell has been urging us to compute lower bounds to the term values, so that they could be bracketed from below as well as from above. In the case of the ground state we were able to establish a gap of 0.5 cm^{-1}, this being smaller by a factor of 10 than the gap previously announced by Kinoshita, but still larger than the experimental uncertainty of 0.15 cm^{-1}. For the 2^3S state the theoretical gap between upper and lower bounds which we obtained was less than the experimental uncertainty in this level.

6. The paper

6. C.L. Pekeris, Excited S States of Helium, Phys. Rev. 127, 509 (1962),

is the first attempt to do spectroscopy from scratch for nonhydrogenic atoms. We have succeeded here in getting term-values up to the ninth excited S-state of Helium. The limit was set by the capacity of our old computer WEIZAC. Our program calls for a determination of all the observed 31 lsns ($n \leq 17$) levels of Helium. With the method having been tried out in every detail, we hope that with our new 1604-A computer, as well as with the use of the 3600 computer during 1963-64, we shall be able to cope with this task, and that the job will be accomplished before the end of 1964.

APPENDIX

Abstracts of Papers Published Under Contract AF61(052)-510 (Nos. 3,4,5 and 6)

1. C.L. Pekeris. Ground State of Two-Electron Atoms. Phys. Rev. 112: 1649 (1958).

A new method is developed for solving the wave equation for two-electron atoms. The wave function is expanded into a triple orthogonal set in three perimetric coordinates. From the wave equation one obtains an explicit recursion relation for the coefficients in the expansion, and the vanishing of the determinant of these coefficients provides the condition for the energy eigenvalues and for the eigenvectors. The determinant was solved on WEIZAC for Z = 1 to 10, using an iteration method. Since the elements of the determinant are integers, and only an average of about 20 per row are nonvanishing, it has been possible to go to an order of 214 before exceeding the capacity of the fast memory of WEIZAC. The nonrelativistic energy eigenvalues obtained for the ground state are lower than any previously published for all Z from 1 to 10. In the case of helium, our nonrelativistic energy value is accurate to within 0.01 cm^{-1} and is 0.40 cm^{-1} lower than the value computed by Kinoshita. From the wave functions obtained, the mass-polarization and the relativistic corrections were evaluated for Z = 1 to 10. Using the values of the Lamb shift computed by Kabir, Salpeter, and Sucher, we obtain an ionization potential for helium of 198 310.67 cm^{-1} as against Herzberg's value of $198\ 310.8_2 \pm 0.15$ cm^{-1}. Comparison is also made with the available experimental data for the other values of Z. By the use of our magnetic tape storage, the accuracy of the nonrelativistic energy value for helium could be pushed to about 0.001 cm^{-1}, should future improvements in the experimental values and in the computed radiative corrections warrant it.

2. C.L. Pekeris. 1^1S and 2^3S States of Helium. Phys. Rev. 115: 1216 (1959).

The method described previously for the solution of the wave equation of two-electron atoms has been applied to the 1^1S and 2^3S states of helium, with the purpose of attaining an accuracy of 0.001 cm^{-1} in the nonrelativistic energy values. For the 1^1S state we have extended our previous calculations by solving determinants of orders 252, 444, 715, and 1078, the last yielding an energy value of -2.903724375 atomic units, with an estimated error of the order of 1 in the last figure. Applying the mass-polarisation and relativistic corrections derived from the new wave functions, we obtain a value for the ionisation energy of 198 312.0258 cm^{-1}, as against the value of 198 312.011 cm^{-1} derived previously from the solution of a determinant of order 210. With a Lamb shift correction of -1.339, due to Kabir, Salpeter, and Sucher, this leads to a theoretical value for the ionisation energy of 198 310.687 cm^{-1}, compared with Herzberg's experimental value of 198 310.8$_2$±0.15 cm^{-1}.

For the 2^3S state we have solved determinants of orders 125, 252, 444, and 715, the last giving an energy value of -2.17522937822 a.u., with an estimated error of the order of 1 in the last figure. This corresponds to a nonrelativistic ionisation energy of 38 453.1292 cm^{-1}. The mass-polarisation and relativistic corrections bring it up to 38 454.8273 cm^{-1}. Using the value of 74.9 ry obtained by Dalgarno and Kingston for the Lamb-shift excitation energy K_0, we get a Lamb-shift correction to the ionisation energy of 2^3S state of -0.16 cm^{-1}. The resulting theoretical value of 38 454.66 cm^{-1} for the ionisation potential is to be compared with the experimental value, which Herzberg estimates to be 38 454.73±0.05 cm^{-1}. The electron density at the nucleus D(0) comes out 33.18416, as against a value of 33.1838±0.00023 which Novick and Commins deduced from the hyperfine splitting. We have also determined expectation values of several positive and negative powers of the three mutual distances, which enter in the expressions for the polarizability and for various sum rules.

3. C.L. Pekeris. 1^1S, 2^1S, and 2^3S States of Li^+. Phys. Rev. 126: 143-145 (1962).

The ionization energy J, excluding the Lamb shift, of the ground state of Li^+ has been evaluated for determinants up to order n = 444. We get J(444) = 610087.449 cm^{-1}, and an extrapolated value J(∞) = 610087.445 cm^{-1}. For the 2^1S state we get a theoretical ionization energy of 118704.88 cm^{-1}, as against the experimental value of 120008.30±0.10 cm^{-1} determined by Herzberg and Moore. It appears that the 8517.4 A line first measured by Series and Willis and later by Herzberg and Moore has been incorrectly identified as the $2^1S - 2^1P$ transition. It should be looked for at 9584 A. For the 2^3S state our value for the ionization energy comes out 134044.12 cm^{-1}, in excellent agreement with the experimental value of 134044.19±0.10 cm^{-1} determined by Herzberg and Moore.

4. C.L. Pekeris, B. Schiff and H. Lifson. Fine Structure of the 2^3P and 3^3P States of Helium. Phys. Rev. 126: 1057-1058 (1962).

Using an extension of the method of Pekeris for S states, eigenvalues and eigenfunctions have been obtained for the 2^1P, 2^3P, 3^1P, and 3^3P states of helium. The fine-structure splittings of the 2^3P and 3^3P states have been computed, including the α^3 quantum electrodynamic correction and the singlet-triplet correction. Determinants up to order n = 220 were solved, and when the results were extrapolated to $n \to \infty$ good agreement was obtained with recent accurate measurements of the fine-structure splittings, substantiating the correctness of the α^3 terms.

5. C.L. Pekeris. 1^1S, 2^1S and 2^3S States of H^- and of He. Phys. Rev. 126: 1470-1476 (1962).

The ionization energy J, including mass-polarization and relativistic corrections but not the Lamb shift correction, was evaluated for the 1^1S state of the negative-hydrogen ion using determinants up to order n = 444. We get J(444) = 6083.0943 cm^{-1}, and, by extrapolation, J(∞) = 6083.0958 cm^{-1}. A search for bound states 2^1S and 2^3S of H^- led to negative results. In the case of helium, an upper bound to the non-relativistic energy eigenvalue ν for the 1^1S state was evaluated at n = 1078 to be $\nu_+ = 198317.866$ cm^{-1}, as against the previously determined lower bound of $\nu_-(1078) = 198317.374$ cm^{-1}. For the 2^3S state this gap is already completely closed at n = 715, with $\nu_+(715) = 38453.1299$ cm^{-1} and $\nu_-(715) = 38453.1292$ cm^{-1}. At n = 1078, J = 38454.827375 cm^{-1}, and the electron charge density at the nucleus D(0) comes out 33.18414092, in agreement with previously extrapolated values. This substantiates a disagreement of the order of one part in 10^5 between theory and experiment in the hyperfine structure of the 2^3S state of He^3 which was established by White, Chow, Drake, and Hughes. With Suh and Zaidi's value for the Lamb shift of -0.109±0.009 cm^{-1}, the ionization energy of the 2^3S state comes out 38454.718±0.009 cm^{-1}, as against Herzberg's experimental value of 38454.73±0.05 cm^{-1}. For the 2^1S state we get J(615) = 32033.318 cm^{-1}, which with a Lamb shift of -0.104±0.014 cm^{-1} evaluated by Suh and Zaidi, leads to an ionization energy of 32033.214 ±0.014 cm^{-1}. The experimental value is, according to Herzberg, equal to 32033.26±0.03 cm^{-1} or, at worst, ±0.05 cm^{-1}. A summary is given of the verification to date of the Lamb shift in two-electron atoms.

6. C.L. Pekeris. The Excited S States of Helium. Phys. Rev. 127: 509-511 (1962).

As part of a program aiming to determine all the observed term-values of two-electron atoms on the basis of the Schrödinger wave equation, we have evaluated the 1s ns levels of helium up to n = 9, in both the singlet and the triplet states. Our previous method, using perimetric coordinates, was extended to allow for the asymmetry between the 1s and the excited electrons. The mass polarization and relativistic corrections were also determined. The difference between the ionization energies J(220), obtained by solving a determinant of order 220, and the experimental values, ranges from 3.6 cm^{-1} for 3^1S to 5.8 cm^{-1} for 9^1S, and from 0.5 cm^{-1} for 3^3S to 5.7 cm^{-1} for 9^3S. The extrapolated values indicate that with a faster computer than WEIZAC it should be feasible to determine all of the 31 observed 1s ns levels ($n \leq 17$) of helium to within the experimental accuracy.

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